

|  |  |   |          |
|--|--|---|----------|
| FORM PTO-1390<br>(REV 11-2000)   |  | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | AT       |
| TRANSMITTAL LETTER TO THE UNITED STATES<br>DESIGNATED/ELECTED OFFICE (DO/EO/US)<br>CONCERNING A FILING UNDER 35 U.S.C. 371 |  |   | 81       |
|  |  |   | US       |
|  |  |   | Nc       |
| INTERNATIONAL APPLICATION NO.<br>PCT/JP00/06075  | INTERNATIONAL FILING DATE<br>September 6, 2000 |   | PR<br>Se |
| TITLE OF INVENTION <b>HYDROGEN GAS GENERATOR AND FUEL CELL SYSTEM USING</b>  |  |   |          |
| APPLICANT(S) FOR DO/EO/US <b>Nobuki MATSUI, Shuji IKEGAMI, Yasunori OKAMOTO, K</b>   |  |   |          |

ib  
data  
correction

Applicant herewith submits to the United States Designated/Elected Office (DO/E) other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a
3. ☒ This is an express request to promptly begin national examination procedi
4. ☐ The US has been elected by the expiration of 19 months from the priority
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☒ has been communicated by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11 to 20 below concern document(s) or information included:**

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

- 1.) Application Data Sheet
- 2.) Five (5) Sheets of Drawings (Figs. 1-5)

|   |  |   |  |                                    |  |
|---|--|---|--|------------------------------------|--|
| U.S. APPLICATION NO. (if known, see 37 CFR 1.50)<br>Not Yet Assigned <b>09/831508</b> |  | INTERNATIONAL APPLICATION NO.<br>PCT/JP00/06075 |  | ATTORNEYS DOCKET NUMBER<br>819-540 |  |
|---|--|---|--|------------------------------------|--|

|   |              |              |           |  |    |  |  |
|---|--------------|--------------|-----------|--|----|--|--|
| 21. <input checked="" type="checkbox"/> The following fees are submitted:<br><b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1) - (5)):</b><br>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO . . . . . \$1000.00<br><br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .. . . . \$860.00<br><br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(3)) paid to USPTO .. . . . \$710.00<br><br>International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) . . . . . \$690.00<br><br>International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) . . . . . \$100.00<br><br><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b> |              |              |           | <b>CALCULATIONS</b><br><br><div style="border: 1px solid black; padding: 5px; min-height: 150px;">                         \$860.00                     </div> |    | <b>PTO USE ONLY</b><br><br><div style="border: 1px solid black; min-height: 150px;"></div> |  |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).   |              |              |           | \$   |    |  |  |
| CLAIMS  | NUMBER FILED | NUMBER EXTRA | RATE      |  |    |  |  |
| Total claims  | 72 - 20 =    | 52           | X \$18.00 | \$ 936.00  |    |  |  |
| Independent claims  | 1 - 3 =      | 0            | X \$80.00 | \$   |    |  |  |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) YES   |              |              |           | + \$270.00   |    |  |  |
| <b>TOTAL OF ABOVE CALCULATIONS =</b>  |              |              |           | \$ 2066.00   |    |  |  |
| <input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2   |              |              |           | \$   |    |  |  |
| <b>SUBTOTAL =</b>   |              |              |           | \$ 2066.00   |    |  |  |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).  |              |              |           | \$   |    |  |  |
| <b>TOTAL NATIONAL FEE =</b>   |              |              |           | \$ 2066.00   |    |  |  |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +  |              |              |           | \$ 40.00   |    |  |  |
| <b>TOTAL FEES ENCLOSED =</b>  |              |              |           | \$ 2106.00   |    |  |  |
|   |              |              |           | Amount to be refunded:   | \$ |  |  |
|   |              |              |           | Charged:   | \$ |  |  |

a. ☒ A check in the amount of \$ 2106.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 19-2380 in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 19-2380 (819-540). A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO

NIXON PEABODY LLP  
8180 Greensboro Drive  
Suite 800  
McLean, Virginia 22102

Donald R. Studebaker

NAME

#32,815

REGISTRATION NUMBER

DRS/sas May 10, 2001

5/PRTS

1

**HYDROGEN GAS GENERATOR  
AND  
FUEL CELL SYSTEM USING SUCH A GENERATOR**

5

**TECHNICAL FIELD**

The present invention relates to a hydrogen gas generator for producing a hydrogen gas from a source fuel of the hydrocarbon family, oxygen, and steam and to a fuel cell system employing such a hydrogen gas generator.

10

**BACKGROUND ART**

It is possible to generate hydrogen by the reforming of hydrocarbon or methanol, and hydrogen gas generators capable of hydrogen generation by such reforming are applicable to fuel cells, hydrogen engines, and the like. Fuel cells are known generally as an electricity generator in which hydrogen delivered as a fuel to the negative electrode and oxygen delivered as an oxidant to the positive electrode react together through an electrolyte.

20

Japanese Patent Gazette No. S58-57361 shows a technique in which either air, air/oxygen, or air/steam is acted on hydrocarbon in the presence of a rhodium catalyst for obtaining hydrogen and CO (carbon monoxide) by partial oxidation. The reaction temperature is from 690 to 900 degrees centigrade. Air and oxygen are used as an oxidant for hydrocarbon and steam is used to generate, by the steam reforming reaction, hydrogen from a fuel which has been left unoxidized in the oxidation reaction. Accordingly, reactions

25

09841508-054004

taking place on the rhodium catalyst when air and steam are acted on hydrocarbon are a partial oxidation reaction and a steam reforming reaction.

Japanese Unexamined Patent Gazette No. S54-76602 shows a technique in which a free oxygen-containing gas is acted on hydrocarbon at a temperature in the range of 815 to 1930 degrees centigrade and under an absolute atmospheric pressure in the range of 1 to 250 ata for generating hydrogen and CO by partial oxidation and, in addition, steams are added for the preheating, dispersion, and transfer of a temperature moderator and hydrocarbon fuel.

Japanese Unexamined Patent Gazette No. H06-92603 shows a technique in which hydrocarbon, oxygen-containing gas, and steam are subjected, under a pressure in the range of 2 from 100 bars and at a temperature in the range of 750 to 1200 degrees centigrade (preferably, in the range of 1000 to 1200 degrees centigrade), to the partial oxidation reaction in the presence of a catalyst for generating hydrogen and CO.

Japanese Unexamined Patent Gazette No. H07-57756 shows a fuel cell electricity generation system having a fuel reformer in which steam is acted on hydrocarbon in the presence of a catalyst for generating hydrogen and CO by a steam reforming reaction. Oxygen is introduced into the fuel reformer to cause, at the same time, the partial oxidation reaction of the hydrocarbon to take place. Since the steam

reformation reaction is endothermic, this compensates for the heat necessary for the steam reformation reaction by making utilization of the partial oxidation reaction which is exothermic.

5 Japanese Unexamined Patent Gazette No. H10-308230 shows a fuel cell electricity generation apparatus comprising a fuel reformer for reforming hydrocarbon into hydrogen by a partial oxidation reaction, a CO shift reactor for causing CO produced in the reforming process to undergo oxidation by a  
10 water gas shift reaction, and a selective oxidization device for subjecting the remaining CO to selective oxidization. This prior art further shows that in addition to the catalyst exhibiting an activity to the partial oxidation reaction, the fuel reformer is filled with another catalyst exhibiting an  
15 activity to the steam reforming reaction of the hydrocarbon. Hydrocarbon, oxygen, and steam are supplied to the reformer to produce hydrogen by the partial oxidation reaction of the hydrocarbon and the steam reforming reaction.

As described above, when performing the reforming of  
20 hydrocarbon into hydrogen by the partial oxidation reaction, it has been known that oxygen and steam are acted on the hydrocarbon in the presence of a catalyst, in which the steam is added for obtaining a steam reforming reaction which is endothermic or for controlling the temperature or the like.

25 This requires that an external heating means with a large

heat transfer area be provided in the fuel reformer in order to maintain the reforming reaction. Moreover, relatively large amounts of CO are generated by the hydrocarbon partial oxidation reaction and the steam reforming reaction.

5 Accordingly, when the presence of CO may be a problem (for example, when the catalyst electrode of a fuel cell must be prevented from undergoing poisoning by CO), a large-size shift reactor is required for the oxidation removal of CO.

As stated in the foregoing patent gazettes (H07-57756 and  
10 H10-308230), with a view to eliminating the need for an external heating means, there is a concept that an absorption of heat by the steam reforming reaction is compensated for by a liberation of heat by the partial oxidation reaction. However, for the case of methane, the heat of reaction of the  
15 steam reforming reaction is about 205 kJ/mol (heat absorption), whereas the heat of reaction of the partial oxidation reaction is only about 36 kJ/mol, and the difference in heat quantity is large. Accordingly, it is practically difficult to eliminate the need for an external  
20 heating means by just employing the concept that steam is added for the purpose of mainly causing a steam reforming reaction to take place.

Accordingly, an object of the present invention is to reduce the external heat quantity required for maintaining  
25 the fuel reforming reaction and to further reduce it to zero.

Furthermore, another object of the present invention is to reduce the amount of CO that is produced by the reforming of fuel and thereby to reduce the load of a CO shift reactor.

Further, still another object of the present invention is to accomplish effective utilization of heat in the entire fuel cell system and to provide a simplified system configuration.

#### DISCLOSURE OF THE INVENTION

In order to accomplish these objects, in the present invention, partial oxidation and water gas shift reactions proceed successively.

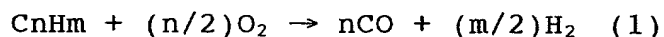
The present invention provides a hydrogen gas generator for generating hydrogen from a source fuel of the hydrocarbon family, oxygen, and steam,

the generator comprising:

a fuel reformer (5) which is provided with a catalyst which exhibits an activity to a partial oxidation reaction of the source fuel;

wherein the source fuel, oxygen, and steam are supplied to the reformer (5) so that the partial oxidation reaction occurs on the catalyst (27) and a water gas shift reaction occurs in which CO produced in the partial oxidation reaction is a reactant.

The above successive reactions are expressed as follows.





The reaction formula (1) is a partial oxidation reaction by which target hydrogen is obtained and CO, which is produced simultaneously with the hydrogen, is oxidized by the water gas shift reaction expressed by the reaction formula (2), during which hydrogen is generated. The addition of steam to the source gas does not much affect the fuel conversion rate in the partial oxidation reaction of the reaction formula (1), but the steam addition makes it easy for the water gas shift reaction of the reaction formula (2) to take place (because the equilibrium inclines toward the generation side), thereby increasing the yield of hydrogen.

The partial oxidation reaction of the reaction formula (1) is an exothermic reaction, and when the source fuel  $\text{C}_n\text{H}_m$  is methane ( $\text{CH}_4$ ),  $\Delta H = -36.07 \text{ kJ/mol}$ . The water gas shift reaction of the reaction formula (2) is also an exothermic reaction, and  $\Delta H = -41.12 \text{ kJ/mol}$ . Accordingly, either the fuel reformer (5) or the source gas (source fuel, oxygen or air, and steam) must be heated up to a certain temperature in order to initiate a reforming reaction. However, once the reaction starts an amount of heat necessary for maintaining the reaction can be obtained from the reaction heat. This reduces the amount of external heating, therefore making it possible to eliminate the need for external heating.



Further, since CO, produced in the partial oxidation reaction of the reaction formula (1), is oxidized by the water gas shift reaction of the reaction formula (2), this reduces the concentration of CO of the reformed gas.

5 Accordingly, even when a CO shift reactor (which is a device capable of oxidation of CO by the water gas shift reaction) and a CO selective oxidation reactor are provided, their load is reduced, so that they can be down sized.

10 It is preferable that the water gas shift reaction is controlled such that the  $\text{CO}_2/\text{CO}$  ratio, which is the ratio of  $\text{CO}_2$  to CO in an outlet gas of the fuel reformer (5), is not less than 0.2. This makes it possible to achieve an increased hydrogen yield.

15 The above point will be made more clear in the description of the following embodiments of the present invention. The fact that the  $\text{CO}_2/\text{CO}$  ratio is high means that the water gas shift reaction is proceeding, whereby hydrogen is produced.

20 The increase in the  $\text{CO}_2/\text{CO}$  ratio, i.e., the proceeding of the water gas shift reaction, relates to the supply rate of source fuel and steam to the fuel reformer (5), and it is therefore preferable that the  $\text{H}_2\text{O}/\text{C}$  ratio, which is the ratio of the number of moles of the steam to the number of moles of carbon of the source fuel, is not less than 0.5.

25 In the present invention, the addition of steam is for the water gas shift reaction, and if the  $\text{H}_2\text{O}/\text{C}$  ratio increases,

this causes the water gas shift reaction to sufficiently proceed. If the ratio is less than 0.5, then the water gas shift reaction will not be proceeded sufficiently. As a result, the CO concentration of a gas obtained increases and  
5 the down-sizing of the CO shift reactor cannot be achieved. Furthermore, the hydrogen yield is not improved.

Further, if the  $H_2O/C$  ratio is increased above 0.5, this ensures that the CO concentration of a reformed gas is positively reduced by the water gas shift reaction. This  
10 prevents the temperature of a CO shift reactor from becoming excessively high. In other words, when the concentration of CO in the reformed gas is high, the CO shift reactor undergoes an excessive increase in its temperature by the water gas shift reaction there (for example, the shift  
15 reactor temperature becomes not less than 100 K above the shift reactor inlet gas temperature). This may result in catalyst sintering or early-stage degradation. However, such is prevented.

It is preferable that the  $H_2O/C$  ratio be not more than 3.  
20 Increasing the  $H_2O/C$  ratio, i.e., increasing the amount of steam, provides the advantage that the water gas shift reaction is promoted. However, an increase in the steam amount requires a large amount of heat corresponding to that increase, therefore resulting in the drop in system total

energy efficiency. Accordingly, the  $H_2O/C$  ratio is set not more than 3.

It is preferable that the outlet gas temperature of the fuel reformer (5) be not more than 800 degrees centigrade.

5 The reason is as follows. As stated above, both the partial oxidation reaction and the water gas shift reaction are an exothermic reaction. Therefore, unlike the steam reforming reaction which is an endothermic reaction, if the reaction temperature becomes excessively high, this provides  
10 disadvantages in the reaction proceeding. It is therefore preferable that the lower limit of the outlet gas temperature be about 450 degrees centigrade. The reason is that if the outlet gas temperature falls below such a lower limit this makes the partial oxidation reaction and the water gas shift  
15 reaction difficult to proceed.

It is preferable that the supply rate of source fuel and oxygen to the fuel reformer (5) is set such that the  $O_2/C$  ratio, which is the ratio of the number of moles of the oxygen to the number of moles of carbon of the source fuel,  
20 is not less than 0.9 times the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction.

The reason for the above setting in which the  $O_2/C$  ratio is set not less than 0.9 times the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction is as follows. Even  
25 when the flow rate (space velocity) of a source gas that is

supplied to the fuel reformer (5) is high, it is possible to provide a high fuel conversion rate (reforming rate). If the  $O_2/C$  ratio is set not less than 0.9 times the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction, then the fuel conversion rate will approach 90%, therefore providing practicability. On the other hand, if the  $O_2/C$  ratio is set not more than 0.9 times the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction, then the fuel conversion rate will not approach 90%, therefore failing to provide practicability.

As can be seen obviously from the reaction formula (1), the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction is 0.5. Therefore, the  $O_2/C$  ratio is not less than 0.45.

If the lower limit of the ratio is set to fall below the theoretical mixture ratio, there is the possibility that a part of the source fuel undergoes a steam reforming reaction. However, the percentage thereof is slight, so that the thermal effect (the temperature drop) on the main reaction (the partial oxidation reaction) is negligible.

Reducing the occurrence of such a steam reforming reaction as rarely as possible can be achieved just by increasing the  $O_2/C$  ratio above the theoretical mixture ratio, in other words, by setting the  $O_2/C$  ratio above than 0.5. However, if the  $O_2/C$  ratio is increased excessively, the complete

oxidation reaction is likely to occur, leading to the drop in the yield of hydrogen. Therefore, the upper limit of the  $O_2/C$  ratio is preferably 1.5 times the  $O_2/C$  theoretical mixture ratio, i.e., about 0.75.

5 As can obviously be seen from the above, it is preferable that the supply rate of source fuel, oxygen, and steam to the fuel reformer (5) is set such that the  $O_2/C$  ratio, which is the ratio of the number of moles of the oxygen to the number of moles of carbon of the source fuel, is not less than 0.9  
10 times the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction, and that the  $H_2O/C$  ratio, which is the ratio of the number of moles of the steam to the number of the source fuel carbon moles, is not less than 0.5.

Further, it is preferable that (a) the supply rate of  
15 source fuel, oxygen, and steam to the fuel reformer (5) is set such that the  $O_2/C$  ratio, which is the ratio of the number of moles of the oxygen to the number of moles of carbon of the source fuel, is not less than 0.9 times but not more than 1.5 times the  $O_2/C$  theoretical mixture ratio in the  
20 partial oxidation and the  $H_2O/C$  ratio, which is the ratio of the number of moles of the steam to the number of the source fuel carbon moles, is not less than 0.5 but not more than 3,  
(b) the water gas shift reaction is controlled such that the  $CO_2/CO$  ratio, which is the ratio of  $CO_2$  to  $CO$  in an outlet  
25 gas of the fuel reformer (5), is not less than 0.2, and (c)

the temperature of the outlet gas of the fuel reformer (5) is not more than 800 degrees centigrade.

As the source fuel of the hydrocarbon family, it is possible to employ propane, natural gas (including LNG), naphtha, kerosene, liquefied petroleum gas (LPG), and city gas, in addition to methane.

As a catalyst metal of the catalyst (27) exhibiting an activity to the partial oxidation reaction, rhodium and ruthenium are preferable. These catalyst metals may be supported on a carrier (support) in the form of a metal simple substance, in the form of an alloy, or in the form of a compound (for example, an oxide). Further, catalyst metals of two or more kinds (for example, rhodium and ruthenium) may be supported on the same carrier. Alternatively, a mixture of catalyst metals of two or more kinds supported on respective carriers may be applicable.

As the carrier, inorganic porous materials whose specific surface area is large are preferable, such as an aluminum oxide.

The catalyst (27) of the carrier carrying thereon a catalyst metal can be filled, in the form of a pellet, to the fuel reformer (5) or may be supported on a monolith carrier by a binder (for example, a honeycomb monolith carrier).

As described above, according to the fuel reformer (5), a gas, whose CO concentration is low, can be obtained. However,

in order to further reduce the CO concentration, an arrangement may be made in which at least one of a CO hot shift reactor, a CO cold shift reactor, and a CO partial oxidation reactor is provided.

5 Another invention of the present application relates to a fuel cell system which is characterized in that it comprises a hydrogen gas generator of the type as described above and a fuel cell (1) which generates electricity using, as its fuel, a hydrogen produced by the hydrogen gas generator.

10 According to this invention, the yield of hydrogen is improved and it is possible to reduce the quantity of external heating necessary for maintaining the reforming reaction and it is also possible to eliminate the need for external heating. Furthermore, the CO concentration of a  
15 reformed gas delivered from the fuel reformer (5) toward the fuel cell is reduced, and even when a CO shift reactor and a CO selective oxidation reactor are provided, their load is reduced, thereby achieving down-sizing.

20 Although the oxygen (or air) and steam of the source gas can be supplied to the fuel reformer (5) from respectively-provided supply sources, the discharged gas of the fuel cell can be utilized instead of using them (oxygen and steam). That is, a gas expelled from the oxygen electrode of the fuel cell contains therein oxygen that has not been used in the  
25 cell reaction and steam produced in the cell reaction. If a

discharged gas supply means for supplying the discharged gas of the oxygen electrode to the fuel reformer (5) is provided, it is then possible to omit the provision of the oxygen (or air) supply source, a steam supply source, and their supply piping. This achieves a simplified fuel cell system configuration. However, another arrangement may be made in which a means for a supply of oxygen (or air) and a means for steam supply are provided separately for a supply of oxygen/steam to the discharged gas of the oxygen electrode.

Further, if an output current control means capable of controlling the output current of the fuel cell is provided, this makes it possible to control the oxygen concentration and the steam concentration of a discharged gas that is supplied to the fuel reformer (5) to fall within their respective given ranges.

That is, the coefficient of fuel (hydrogen) utilization and the coefficient of oxygen (air) utilization in a fuel cell vary with the load (the amount of electric power used) of the fuel cell. In other words, when the amount of fuel flowing into the fuel cell and the amount of oxygen flowing into the fuel cell are fixed, if the output current value of the cell is varied, the amounts of hydrogen and oxygen that are consumed in the cell reaction vary. This is accompanied with a change in the amount of steam. Accordingly, by controlling the output current value, it becomes possible to supply to



the fuel reformer (5) a discharged gas with a given oxygen concentration and a given steam concentration that are suitable for the reforming of fuel.

In the fuel cell, the output current is controlled such that the oxygen utilization coefficient preferably ranges between 0.4 and 0.75 (40-75% of the amount of oxygen supplied). Because of this, it is possible to control the  $H_2O/C$  ratio of a source gas for the fuel reformer (5) to range between about 0.67 and about 3.0.

That is, in the fuel cell the amount of steam produced is theoretically two times the amount of oxygen consumed ( $O_2 + 2H_2 \rightarrow 2H_2O$ ), so that if the oxygen utilization coefficient is 0.4, an amount of steam equivalent to twice the oxygen utilization coefficient (i.e., 0.8) is produced, and the residual oxygen amount is an equivalent amount of 0.6. Therefore, the  $H_2O/O_2$  ratio of the discharged gas is (0.8/0.6). If the amount of supply of the discharged gas to the fuel reformer (5) is controlled such that the  $O_2/C$  ratio of a source gas is a stoichiometric ratio of 0.5, then the  $H_2O/C$  ratio of the source gas is as follows.

$$H_2O/C \text{ ratio} = 0.5 \times (0.8/0.6) = \text{about } 0.67$$

Likewise, the following calculation is carried out for the oxygen utilization coefficient = 0.75.

$$H_2O/C \text{ ratio} = 0.5 \times (1.5/0.25) = 3$$

As described above, in accordance with the fuel reformer, a reformed gas, whose CO concentration is low, can be obtained. However, in order to further reduce the CO concentration, an arrangement may be made in which at least one of a CO hot shift reactor, a CO cold shift reactor, and a CO partial oxidation reactor is provided and the reformed gas is passed therethrough and supplied to the fuel cell.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a diagram showing how a hydrogen gas generator according to an embodiment of the present invention and a fuel cell system employing such a hydrogen gas generator are configured.

Figure 2 shows in cross section structures of a fuel reformer and a combustor of the fuel cell system.

Figure 3 graphically shows a relationship between the  $H_2O/C$  ratio of a source gas, the  $CO_2/CO$  ratio of a reformed gas, and the hydrogen yield ratio.

Figure 4 is a diagram showing how a fuel cell system according to another embodiment of the present invention is configured.

Figure 5 graphically shows a relationship between the fuel utilization coefficient and the fuel conversion rate at which the energy efficiency of the fuel cell system reaches a maximum.

#### BEST MODE FOR CARRYING OUT THE INVENTION

In order to describe the present invention in detail, the description thereof will be made by making reference to the accompanying drawings. The following are main reference numerals in the drawings.

5        1: FUEL CELL

         2: OXYGEN ELECTRODE

         3: HYDROGEN ELECTRODE

         4: AIR COMPRESSOR (AIR SUPPLY)

         5: FUEL REFORMER

10       7: CO HOT SHIFT REACTOR

         14: WATER TANK (STEAM SUPPLY)

         27: CATALYST

         35: DISCHARGED GAS SUPPLY PIPE (DISCHARGED GAS SUPPLY  
MEANS)

15       38: POWER CONTROLLER (OUTPUT CURRENT CONTROL MEANS)

         39: FLOW RATE CONTROL VALVE (AIR SUPPLY MEANS)

         40: WATER SUPPLY PIPE (STEAM SUPPLY MEANS)

         60: HYDROGEN GAS GENERATOR

First, the entire fuel cell system will be described below.

20       Figure 1 shows a configuration of the fuel cell system of the present invention, in which the reference numeral 1 denotes a fuel cell of the solid polyelectrolyte type having an oxygen electrode (cathode) 2 which is a catalyst electrode and a hydrogen electrode (anode) 3 which is also a catalyst  
25       electrode. An air compressor 4 is connected to the oxygen

electrode 2 by an air supply pipe 10. A fuel reformer 5 is connected to the hydrogen electrode 3 by a reformed gas supply pipe 20. In the reformed gas supply pipe 20 are a first heat exchanger 6, a CO hot shift reactor 7, a second heat exchanger 8, a CO cold shift reactor 9, a third heat exchanger 11, a CO selective oxidation reactor 12, and a fourth heat exchanger 13 which are disposed in that order in the direction toward the fuel cell 1.

A source gas supply pipe 30 establishes connection between the fuel reformer 5 and a source fuel supply (city gas) 14. A gas compressor 15 and a desulfurizer 16 are disposed in the source gas supply pipe 30 in that order in the direction toward the fuel reformer 5. Moreover, a pipe, branched off from the air supply pipe 10, is connected to the fuel reformer 5 so that air for the partial oxidation reaction is supplied from the air compressor 4 to the fuel reformer 5, and the fuel reformer 5 and a water tank 17 are connected together by a supply pipe 40 so that water for obtaining steam for the water gas shift reaction is supplied, in an atomized form, to the fuel reformer 5. Disposed in the water supply pipe 40 is a pump 18.

The source fuel from the source fuel supply 14, the air from the air compressor 4, and the steam from the water tank 17 are heated by the combustor 19 and supplied to the fuel reformer 5. Further, connected to a portion of the reformed

gas supply pipe 20 located upstream of the first heat exchanger 6 is a pipe which is branched off from the water supply pipe 40 for a supply of water in an atomized form to obtain steams for the water gas shift reaction. Connected to  
 5 a portion of the reformed gas supply pipe 20 located upstream of the third heat exchanger 11 is a pipe which branched off from the air supply pipe 10 for a supply of air for the selective oxidation reactor 12.

In the above, the air compressor 4, the fuel reformer 5,  
 10 the CO hot shift reactor 7, the CO cold shift reactor 9, the selective oxidation reactor 12, the heat exchangers 6, 8 and 11, the source fuel supply 14, the gas compressor 15, the desulfurizer 16, the water tank 17, the pump 18, the combustor 19, and each piping 10, 20, 30 and 40 together form  
 15 a hydrogen gas generator 60 of the present invention.

It is arranged such that discharged gases from the oxygen and hydrogen electrodes 2 and 3 of the fuel cell 1 are passed through steam separators 21 and 22. Thereafter, these gases are merged together and supplied, through a gas pipe 50, to  
 20 the combustor 19 as a gas for combustion. The discharged gas of the oxygen electrode 2 can suitably be vented by a valve 23 to atmosphere. The gas pipe 50 is so laid out as to pass through the fourth heat exchanger 13, through the third heat exchanger 11, and through the second heat exchanger 8 in that  
 25 order, and the discharged gas is heated by heat exchange with

the reformed gas in each heat exchanger and supplied to the combustor 19. Accordingly, the reformed gas is, on the contrary, cooled in each heat exchanger and supplied to the fuel cell 1. Another cooled water pipe 24 passes through the first heat exchanger 6 and the reformed gas is cooled by heat exchange with the cooled water flowing through the cooled water pipe 24.

The fuel reformer 5 is filled with a catalyst (which is formed of  $\text{Al}_2\text{O}_3$  carrying thereon either Ru or Rh) that exhibits an activity to the partial oxidation reaction. The CO hot shift reactor 7 is filled with a catalyst, such as  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ , that exhibits an activity to the water gas shift reaction at high temperatures (400 degrees centigrade or thereabouts). The CO cold shift reactor 9 is filled with a catalyst, such as CuO and ZnO, that exhibits an activity to the water gas shift reaction at low temperatures (180 degrees centigrade or thereabouts). The CO selective oxidation reactor 12 is filled with a catalyst (which is formed of  $\text{Al}_2\text{O}_3$  or zeolite carrying thereon Ru or Pt) that exhibits an activity to the selective oxidation reaction. The combustor 19 is filled with a combustion catalyst. Furthermore, the fuel reformer 5 is provided with an electric heater for pre-heating.

Referring to Figure 2, there is shown a reactor 25 which is an integration of the fuel reformer 5 and the combustor 19.

In the reactor 25 of Figure 2, an electric heater 26 is incorporated between the upper-side fuel reformer 5 and the lower-side combustion 19. A site of the fuel reformer 5 is filled with a honeycomb catalyst 27 of a honeycomb monolith carrier carrying thereon a catalyst. A site of the combustion 19 is filled with a combustion catalyst 28, and a source gas passage 29 extends from a source gas inlet 31 at the lower end to where the electric heater is disposed, passing through the catalyst-filled site of the combustor 19. Moreover, in Figure 2, the reference numeral 32 denotes a reformed gas outlet, the reference numeral 33 denotes an inlet of the discharged gas from the fuel cell 1, and the reference numeral 34 denotes a combusted/discharged gas outlet.

In the above-described fuel cell system, the temperature of the fuel reformer 5 when the system is started is low, so that the electric heater is operated until the temperature is increased to such an extent that the catalyst becomes active, for example, about 460 degrees centigrade. After the system is started, the electric heater is turned off, and a source gas (source fuel and a mixed gas of air and steam) is pre-heated only in the combustor 19. The source gas is controlled such that the  $H_2O/C$  ratio ranges between 0.5 to 3 and the  $O_2/C$  ratio ranges between 0.45 and 0.75, by controlling the supply amount of source fuel, air, and steam.

The outlet gas temperature of the fuel reformer 5 is separately controlled so as not to go beyond 800 degrees centigrade. A most preferable operating condition is as follows. That is, the  $H_2O/C$  ratio is 1.0, the  $O_2/C$  ratio is from 0.52 to 0.60 (more preferably, 0.56), the outlet gas temperature of the fuel reformer 5 is 720 degrees centigrade, and the  $CO_2/CO$  ratio of the outlet gas of the fuel reformer 5 is 0.4.

After desulfurization, the source fuel is heated together with air and atomized water, by the electric heater or the combustor 19 and supplied to the catalyst of the fuel reformer 5. The atomized water is changed to steams by such heating. The partial oxidation reaction of the source fuel occurs on the catalyst of the fuel reformer 5, thereby producing hydrogen and CO (see Formula (1)). Since there exist steams in the inside of the fuel reformer 5, this causes, at the same time, a water gas shift reaction to take place, as a result of which hydrogen and carbon dioxide are generated, and the CO concentration is reduced (see Formula (2) ).

Leaving the fuel reformer 5, the reformed gas is cooled down to about 400 degrees centigrade in the first heat exchanger 6 and delivered to the CO hot shift reactor 7 where the CO concentration is further reduced by a water gas shift reaction taking place on the catalyst of the shift reactor 7.



Then, leaving the CO hot shift reactor 7, the reformed gas is further cooled down to about 180 degrees centigrade in the second heat exchanger 8 and supplied to the CO cold shift reactor 9 where the CO concentration is further reduced by a water gas shift reaction taking place on the catalyst of the shift reactor 9. Then, leaving the CO cold shift reactor 9, the reformed gas is cooled down to about 140 degrees centigrade in the third heat exchanger 11 and supplied to the CO selective oxidation reactor 12 where the CO concentration is further reduced by a water gas shift reaction taking place on the catalyst of the reactor 12. Leaving the CO selective oxidation reactor 12, the reformed gas is cooled down to about 80 degrees centigrade in the fourth heat exchanger 13 and supplied to the hydrogen electrode 3 of the fuel cell 1.

In the fuel cell 1, a cell reaction of  $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$  occurs at the surface of the hydrogen electrode 3 and a cell reaction of  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$  occurs at the surface of the oxygen electrode 2. Therefore, a discharged gas from the oxygen electrode 2 contains therein residual air that has not been used in the cell reaction and steams produced by the cell reaction. On the other hand, contained in a discharged gas from the hydrogen electrode 3 are hydrogen that has not been used in the cell reaction, non-reformed source fuel, air, and steam.

The discharged gases of the oxygen and hydrogen electrodes 2 and 3 pass through the steam separators 21 and 22 and are merged together. Thereafter, the discharged gas thus merged is heated by heat exchange in the fourth, third and second 5 heat exchangers 13, 11, and 8 and delivered to the combustor 19.

The discharged gas contains hydrogen and oxygen which undergo a reaction by the action of the combustion catalyst in the combustor 19, and the resulting reaction heat becomes 10 a preheating supply for the source gas. On the other hand, the non-reformed source material contained in the discharged gas is burned at the same time to become a preheating supply.

Next, the relationship between  $H_2O/C$  ratio,  $CO_2/CO$  ratio, and hydrogen yield ratio will be described below.

Referring to Figure 3, there is shown a relationship 15 between the  $H_2O/C$  ratio of a source gas that is introduced into the fuel reformer 5 (i.e., the ratio of the number of moles of steam to the number of moles of carbon in a source fuel), the  $CO_2/CO$  ratio of a reformed gas from the fuel reformer 5 (i.e., the ratio of  $CO_2$  to  $CO$  in a reformer outlet 20 gas), and the hydrogen yield ratio by the fuel reformer 5 (i.e., the ratio in which the hydrogen yield is 1 when  $H_2O/C$  ratio = 0.5). The operation condition of the fuel reformer 5 is as follows. The inlet gas temperature is 460 degrees 25 centigrade. The  $O_2/C$  ratio (i.e., the ratio of the number of

moles of oxygen to the number of moles of carbon of a source fuel) is 0.56. The gas pressure is 150 kPa.

According to Figure 3, as the  $H_2/C$  ratio increases, the  $CO_2/CO$  ratio likewise increases. The fact that the  $CO_2/CO$  ratio is great means that CO changes to  $CO_2$  in the fuel reformer 5. This change is attributed to the complete oxidation reaction of the source fuel as well as to the water gas shift reaction of CO. It is proved that the addition of steams makes it possible to cause the water gas shift reaction to efficiently proceed in the fuel reformer 5, for it is not conceivable that the increase in the  $H_2/CO$  ratio (i.e., the increase in the amount of steam) makes the complete oxidation reaction easy to proceed.

Figure 3 shows that the hydrogen yield increases if the  $H_2/C$  ratio is not less than 0.5. The hydrogen yield increases if the water gas shift reaction in the fuel reformer 5 is so controlled as to increase the  $CO_2/CO$  ratio above 0.2. In other words, the hydrogen yield can be increased by controlling the source gas composition, the reaction temperature or others.

Next, the effect of the type of the catalyst 27 of the fuel reformer 5 on the reformed gas composition will be explained.

Referring to Table 1, there is shown a relationship between the inlet gas composition (the source gas composition) and the outlet gas composition (the reformed gas composition) of

the fuel reformer 5 when fuel reforming was carried out employing different catalysts for use in the fuel reformer 5. Three types of catalysts, i.e., Ni-Al<sub>2</sub>O<sub>3</sub> (formed of Al<sub>2</sub>O<sub>3</sub> carrying thereon Ni), Rh-Al<sub>2</sub>O<sub>3</sub> (formed of Al<sub>2</sub>O<sub>3</sub> carrying thereon Rh), and Ru-Al<sub>2</sub>O<sub>3</sub> (formed of Al<sub>2</sub>O<sub>3</sub> carrying thereon Ru), were used.

TABLE 1

| CATALYST TYPE                     | GAS                  | INLET COMPOSITION | OUTLET COMPOSITION |
|-----------------------------------|----------------------|-------------------|--------------------|
| Ni-Al <sub>2</sub> O <sub>3</sub> | H <sub>2</sub>       | -                 | 0.3071             |
|                                   | N <sub>2</sub>       | 0.4637            | 0.4728             |
|                                   | CH <sub>4</sub>      | 0.2200            | 0.0549             |
|                                   | CO                   | -                 | 0.1063             |
|                                   | CO <sub>2</sub>      | -                 | 0.0590             |
|                                   | O <sub>2</sub>       | 0.1233            | -                  |
|                                   | H <sub>2</sub> O     | 0.1931            | -                  |
|                                   | SV(h <sup>-1</sup> ) | 143000            | -                  |
| Rh-Al <sub>2</sub> O <sub>3</sub> | H <sub>2</sub>       | -                 | 0.3704             |
|                                   | N <sub>2</sub>       | 0.4638            | 0.4301             |
|                                   | CH <sub>4</sub>      | 0.2199            | 0.0168             |
|                                   | CO                   | -                 | 0.1261             |
|                                   | CO <sub>2</sub>      | -                 | 0.0566             |
|                                   | O <sub>2</sub>       | 0.1233            | -                  |
|                                   | H <sub>2</sub> O     | 0.1930            | -                  |
|                                   | SV(h <sup>-1</sup> ) | 143000            | -                  |
| Ru-Al <sub>2</sub> O <sub>3</sub> | H <sub>2</sub>       | -                 | 0.3649             |
|                                   | N <sub>2</sub>       | 0.4638            | 0.4330             |
|                                   | CH <sub>4</sub>      | 0.2199            | 0.0215             |
|                                   | CO                   | -                 | 0.1211             |
|                                   | CO <sub>2</sub>      | -                 | 0.0596             |
|                                   | O <sub>2</sub>       | 0.1233            | -                  |
|                                   | H <sub>2</sub> O     | 0.1930            | -                  |
|                                   | SV(h <sup>-1</sup> ) | 143000            | -                  |

10 As can be seen from Table 1, for the case of the Rh-Al<sub>2</sub>O<sub>3</sub> catalyst and the Ru-Al<sub>2</sub>O<sub>3</sub> catalyst, the rate of conversion of methane into hydrogen is high, whereas for the case of the

Ni-Al<sub>2</sub>O<sub>3</sub> catalyst the conversion rate is low. From this, it is preferable to employ in the fuel reformer 5 either the Rh-Al<sub>2</sub>O<sub>3</sub> catalyst or the Ru-Al<sub>2</sub>O<sub>3</sub> catalyst.

Next, the effect of the H<sub>2</sub>O/C ratio on the reformed gas composition in the Rh-Al<sub>2</sub>O<sub>3</sub> catalyst will be explained.

Referring to Table 2, there is shown a relationship between the inlet gas composition (the source gas composition) and the outlet gas composition (the reformed gas composition) of the fuel reformer 5 when the Rh-Al<sub>2</sub>O<sub>3</sub> catalyst was employed in the fuel reformer 5, and fuel reforming was carried out at different H<sub>2</sub>O/C ratios.

09831508-051001  
TOTAL 508

Table 2

| CATALYST<br>TYPE                  | GAS                  | INLET<br>COMPOSITION | OUTLET<br>COMPOSITION |
|-----------------------------------|----------------------|----------------------|-----------------------|
| Rh-Al <sub>2</sub> O <sub>3</sub> | H <sub>2</sub>       | -                    |                       |
|                                   | N <sub>2</sub>       | 0.4637               | 0.3913                |
|                                   | CH <sub>4</sub>      | 0.2199               |                       |
|                                   | CO                   | -                    | 0.4161                |
|                                   | CO <sub>2</sub>      | -                    |                       |
|                                   | O <sub>2</sub>       | 0.1233               | 0.0086                |
|                                   | H <sub>2</sub> O     | 0.1931               |                       |
|                                   | SV(h <sup>-1</sup> ) | 29000                | 0.1175                |
|                                   | .....                | .....                |                       |
|                                   | H <sub>2</sub>       | -                    | 0.0665                |
|                                   | N <sub>2</sub>       | 0.3758               |                       |
|                                   | CH <sub>4</sub>      | 0.1781               | -                     |
|                                   | CO                   | -                    | -                     |
|                                   | CO <sub>2</sub>      | -                    | -                     |
|                                   | O <sub>2</sub>       | 0.0999               |                       |
|                                   | H <sub>2</sub> O     | 0.3462               | -                     |
|                                   | SV(h <sup>-1</sup> ) | 29000                | .....                 |
|                                   |                      |                      | 0.4121                |
|                                   |                      |                      | 0.4029                |
|                                   |                      |                      | 0.0073                |
|                                   |                      |                      | 0.0805                |
|                                   |                      |                      | 0.0973                |
|                                   |                      |                      | -                     |
|                                   |                      |                      | -                     |
|                                   |                      |                      | -                     |

As can be seen from Table 2, as the H<sub>2</sub>O/C ratio increases, the CO<sub>2</sub>/CO ratio increases and the hydrogen yield also increases. This agrees with the result shown in Figure 3.

Next, another embodiment of the fuel cell system of the present invention will be described below.

Referring to Figure 4, there is shown another embodiment of the fuel cell system of the present invention. The present fuel cell system differs from the first fuel cell system. First, instead of introducing to the fuel reformer 5 air from the air compressor 4 and water from the water tank 17, the discharged gas of the oxygen electrode 2 is supplied through a supply pipe 35 to the fuel reformer 5. Second, another power supply 37 and the fuel cell 1 are connected in parallel to an electric load 36 and a power controller 38 for controlling the output current value of the fuel cell 1 is disposed. Finally, a flow rate control valve 39 is disposed in a branch pipe extendedly arranged from the air supply pipe 10 toward the source gas supply pipe 30 to form an air supply means.

As described above, the discharged gas of the oxygen electrode 2 contains steams and unused air. The discharged gas is therefore used as a gas for source fuel reforming in the fuel reformer 5 and the power controller 38 is disposed to make the composition of the discharged gas suitable for fuel reforming. By controlling the output current value of the fuel cell 1 with the power controller 38, the coefficient of utilization of hydrogen and air of the fuel cell 1 varies and, as a result, the oxygen concentration and the steam concentration of the discharged gas of the oxygen electrode 2

vary. The lack of electric power resulting from such control is supplemented by the power supply 37.

If the coefficient of utilization of hydrogen is 100% when the amount of hydrogen used in the fuel cell 1 is 1L/min (0 °C and 1 atmospheric pressure), then the output current value A at that time is theoretically as follows.

$$A = 2 nF$$

$$= 143 \text{ (ampere)}$$

(A: C(coulomb)/sec; n: mole/sec; and F: Faraday constant)

Accordingly, if the output current value is decreased below the above theoretical value, then both the hydrogen utilization coefficient (the fuel utilization coefficient) and the air utilization coefficient decrease. In this case, the air utilization coefficient is so controlled to fall in the range, for example, between 0.4 and 0.75.

Further, the lack of air when the air utilization coefficient is increased is supplemented by introducing air from the air compressor 4 by the flow rate control valve 39.

Next, the relationship between fuel utilization coefficient and fuel conversion rate will be explained.

Figure 5 graphically shows a relationship between the fuel utilization coefficient of the fuel cell 1 and the fuel conversion rate of the fuel reformer 5 at which the energy efficiency reaches a maximum in a fuel cell system which uses a source fuel which has not been reformed and a hydrogen



which has not been used of the source fuel supplied from the source fuel supply 14 for fuel gas preheating.

For example, when the fuel conversion rate is 0.94, the fuel utilization coefficient, at which the energy efficiency reaches a maximum, is 0.98. In this example, 6% of the source fuel that has been remained unreformed and 2% of the hydrogen in the reformed gas that has been remained unused in the cell reaction were utilized for source gas preheating.

In each of the embodiments of the present invention, the combustor 19 is provided, wherein the discharged gas of the fuel cell 1 is utilized for source gas preheating. An arrangement may be made in which the provision of the combustor 19 is omitted and the discharged gas is burned in the catalyst to provide another heat supply. The reason is that since both the partial oxidation reaction and the water gas shift reaction occurring in the fuel reformer 5 are exothermic, the reaction temperature is maintained by the exothermic reaction heat after the fuel reformer 5 is heated up to the reaction temperature by the electric heater at the start.

## CLAIMS

## WHAT IS CLAIMED IS:

1. A hydrogen gas generator for generating hydrogen from a source fuel of the hydrocarbon family, oxygen, and steam,

5 said hydrogen gas generator comprising:

a fuel reformer (5) with a catalyst (27) which exhibits an activity to a partial oxidation reaction of said source fuel;

10 wherein said source fuel, oxygen, and steam are supplied to said reformer (5) so that said partial oxidation reaction occurs on said catalyst (27) and a water gas shift reaction occurs in which CO produced in said partial oxidation reaction is a reactant.

15 2. The hydrogen gas generator of claim 1, wherein said water gas shift reaction is controlled such that the  $\text{CO}_2/\text{CO}$  ratio, which is the ratio of  $\text{CO}_2$  to CO in an outlet gas of said fuel reformer (5), is not less than 0.2.

20 3. The hydrogen gas generator of claim 1, wherein the supply rate of source fuel and steam to said fuel reformer is set such that the  $\text{H}_2\text{O}/\text{C}$  ratio, which is the ratio of the number of moles of said steam to the number of moles of carbon of said source fuel, is not less than 0.5.

4. The hydrogen gas generator of claim 3, wherein the  $\text{H}_2\text{O}/\text{C}$  ratio is not more than 3.

5. The hydrogen gas generator of claim 1, wherein the outlet gas temperature of said fuel reformer (5) is not more than 800 degrees centigrade.

6. The hydrogen gas generator of claim 1, wherein the  
5 supply rate of source fuel and oxygen to said fuel reformer (5) is set such that the  $O_2/C$  ratio, which is the ratio of the number of moles of said oxygen to the number of moles of carbon of said source fuel, is not less than 0.9 times the  $O_2/C$  theoretical mixture ratio in said partial oxidation  
10 reaction.

7. The hydrogen gas generator of claim 1, wherein the supply rate of source fuel and oxygen to said fuel reformer (5) is set such that the  $O_2/C$  ratio, which is the ratio of the number of moles of said oxygen to the number of moles of  
15 carbon of said source fuel, is greater than said  $O_2/C$  theoretical mixture ratio in said partial oxidation reaction.

8. The hydrogen gas generator of claim 6, wherein said  $O_2/C$  is not more than 1.5 times said  $O_2/C$  theoretical mixture ratio

20 9. The hydrogen gas generator of claim 1, wherein the supply rate of source fuel, oxygen, and steam to said fuel reformer (5) is set such that the  $O_2/C$  ratio, which is the ratio of the number of moles of said oxygen to the number of moles of carbon of said source fuel, is not less than 0.9  
25 times said  $O_2/C$  theoretical mixture ratio in said partial

oxidation reaction, and that the  $H_2O/C$  ratio, which is the ratio of the number of moles of said steam to the number of said source fuel carbon moles, is not less than 0.5.

10. A hydrogen gas generator for generating hydrogen from  
5 a source fuel of the hydrocarbon family, oxygen, and steam,  
said hydrogen gas generator comprising:

a fuel reformer (5) with a catalyst (27) which exhibits an activity to a partial oxidation reaction of said source fuel;

wherein the supply rate of source fuel, oxygen, and steam  
10 to said fuel reformer (5) is set such that the  $O_2/C$  ratio,  
which is the ratio of the number of moles of said oxygen to  
the number of moles of carbon of said source fuel, is not  
less than 0.9 times but not more than 1.5 times the  $O_2/C$   
theoretical mixture ratio in said partial oxidation, and that  
15 the  $H_2O/C$  ratio, which is the ratio of the number of moles of  
said steam to the number of said source fuel carbon moles, is  
not less than 0.5 but not more than 3, whereby said partial  
oxidation reaction occurs on said catalyst and a water gas  
shift reaction occurs in which CO produced in said partial  
20 oxidation reaction is a reactant;

wherein said water gas shift reaction is controlled such  
that the  $CO_2/CO$  ratio, which is the ratio of  $CO_2$  to CO in an  
outlet gas of said fuel reformer (5), is not less than 0.2;  
and

wherein the temperature of said outlet gas of said fuel reformer (5) is not more than 800 degrees centigrade.

11. The hydrogen gas generator of claim 1, wherein an active site of said catalyst (27) is formed of at least one  
5 of rhodium and ruthenium.

12. The hydrogen gas generator of claim 11, wherein said catalyst (27) is supported on a honeycomb monolith carrier

13. A fuel cell system comprising:

a hydrogen gas generator of any one of claims 1-12; and

10 a fuel cell (1) capable of generating electricity by making use of hydrogen produced by said hydrogen gas generator as a fuel.

14. The fuel cell system of claim 13 further comprising:

discharged gas supply means (35) for supplying a steam-  
15 containing gas, discharged from an oxygen electrode of said fuel cell, to said fuel reformer (5) for a supply of steam to said fuel reformer (5).

15. The fuel cell system of claim 13 further comprising:

output current control means (38) for controlling the  
20 output current of said fuel cell so that the oxygen concentration and the steam concentration of a discharged gas that is supplied to said fuel reformer (5) fall within their respective given ranges.

16. The fuel cell system of claim 13 further comprising:

output current control means for controlling the output current of said fuel cell so that the coefficient of utilization of oxygen of said fuel cell ranges from 0.4 to 0.75.

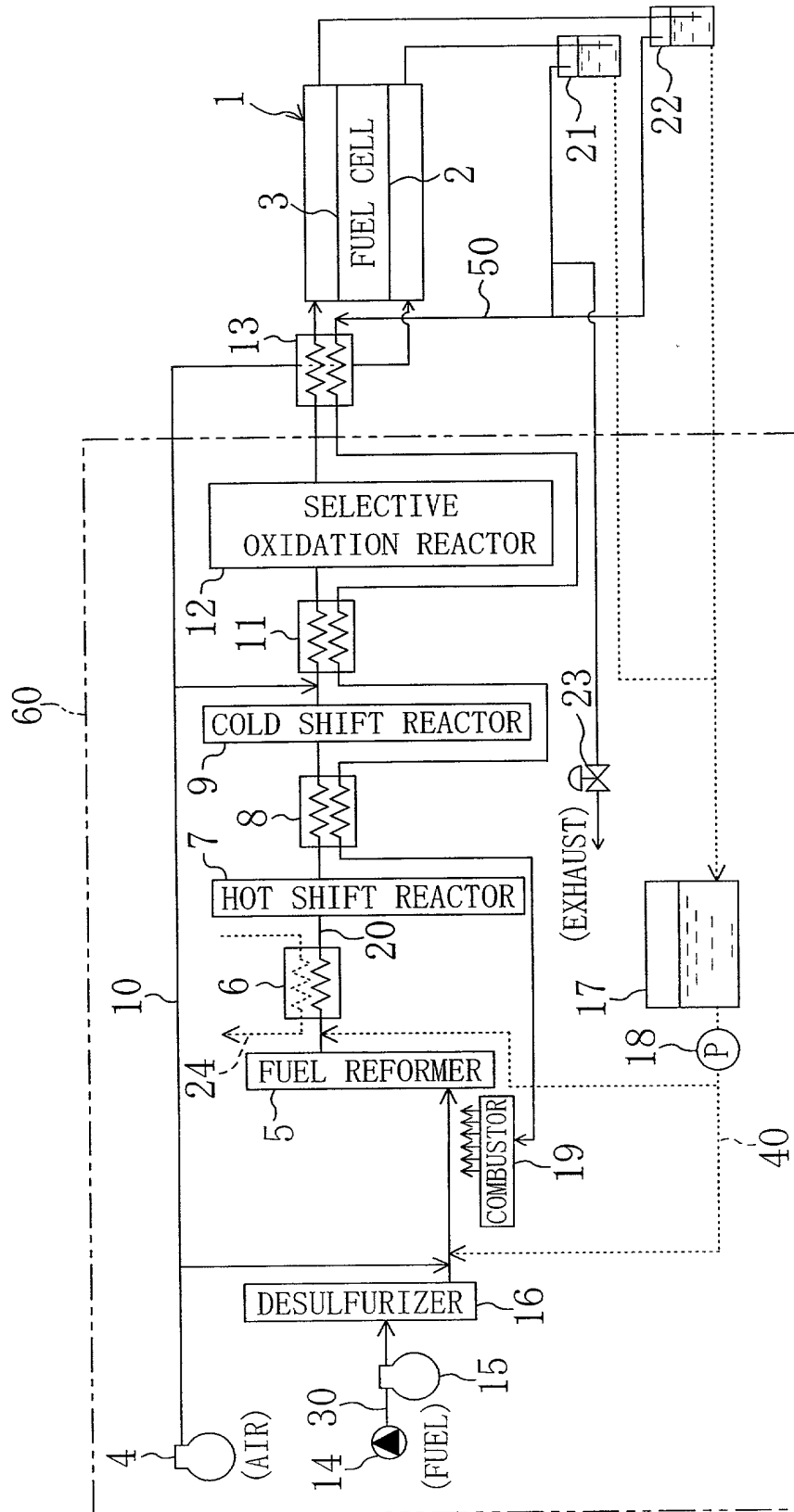
- 5     17. The fuel cell system of claim 13 further comprising:  
air supply means (39) for a supply of air to said fuel reformer (5).

05831509-054001

**ABSTRACT**

Placed in a fuel reformer (5) is a catalyst (27) which exhibits an activity to the partial oxidation reaction of a source fuel. The source fuel, oxygen, and steam are supplied to the fuel reformer (5) such that the ratio  $O_2/C$ , i.e., the ratio of the number of moles of the oxygen to the number of moles of carbon of the source fuel, is not less than 0.9 times the  $O_2/C$  theoretical mixture ratio in the partial oxidation reaction, and the  $H_2O/C$  ratio, i.e., the ratio of the number of moles of the steam to the number of the source fuel carbon moles is not less than 0.5, wherein the partial oxidation reaction occurs in the catalyst (27) to cause a water gas shift reaction to take place in which CO produced by the partial oxidation reaction is a reactant, for generation of hydrogen.

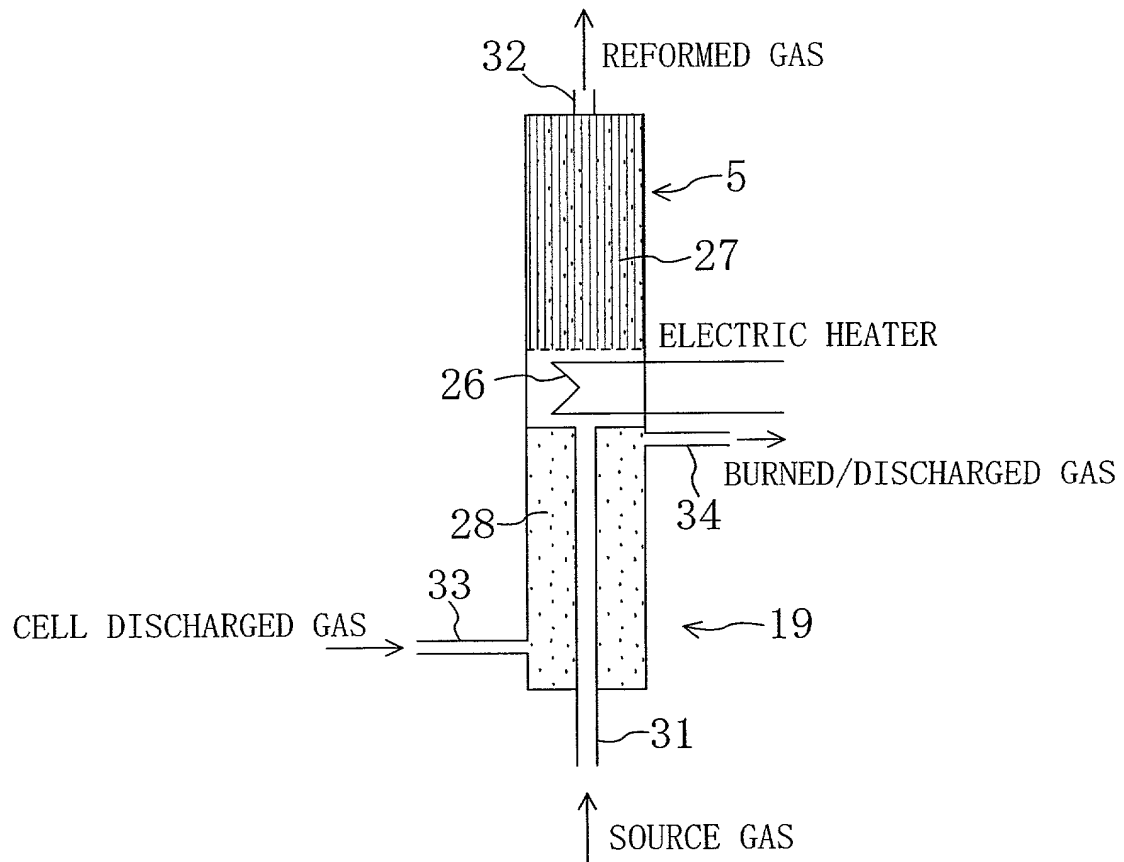
Fig. 1





2/5

Fig. 2



3/5

Fig. 3

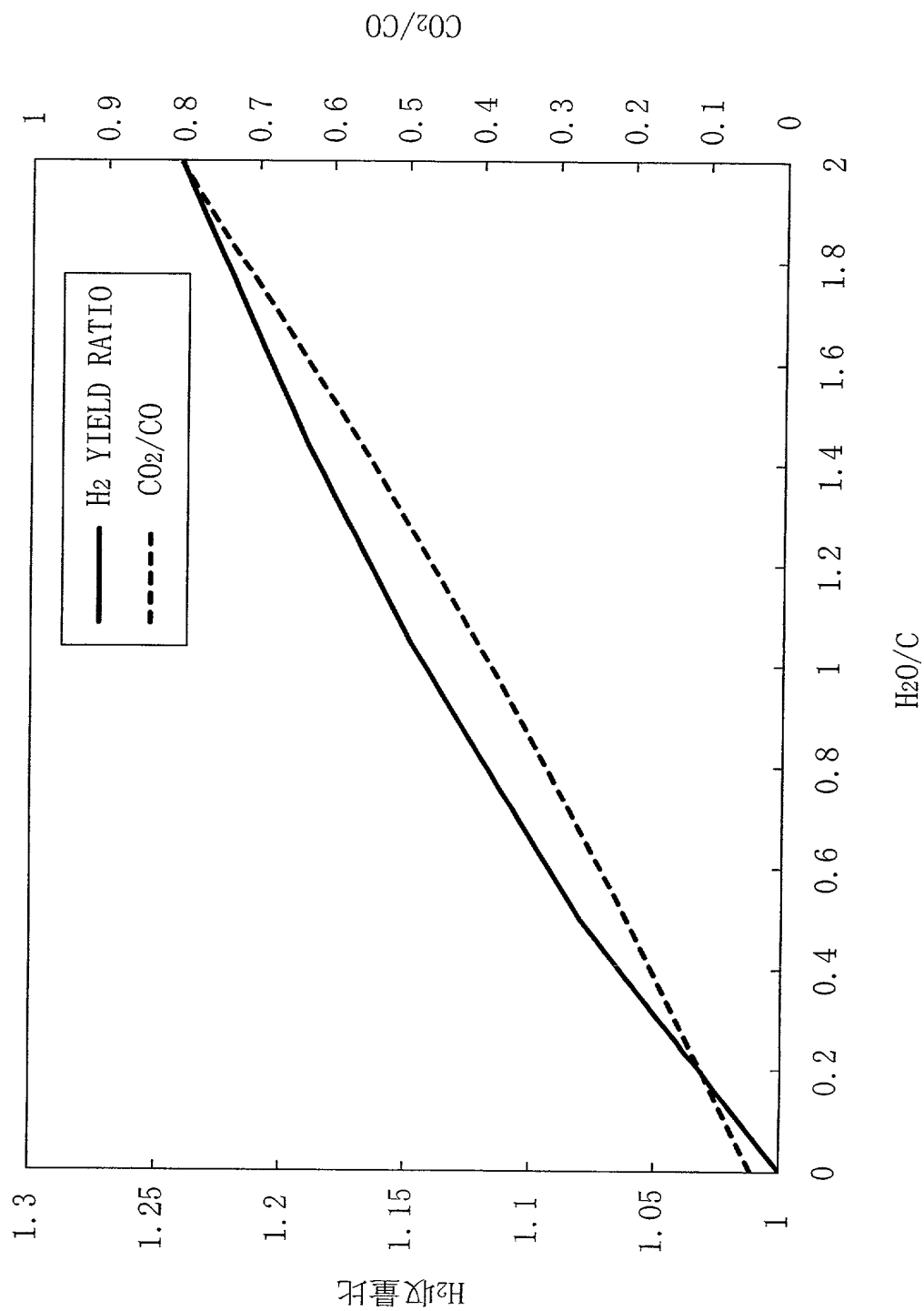
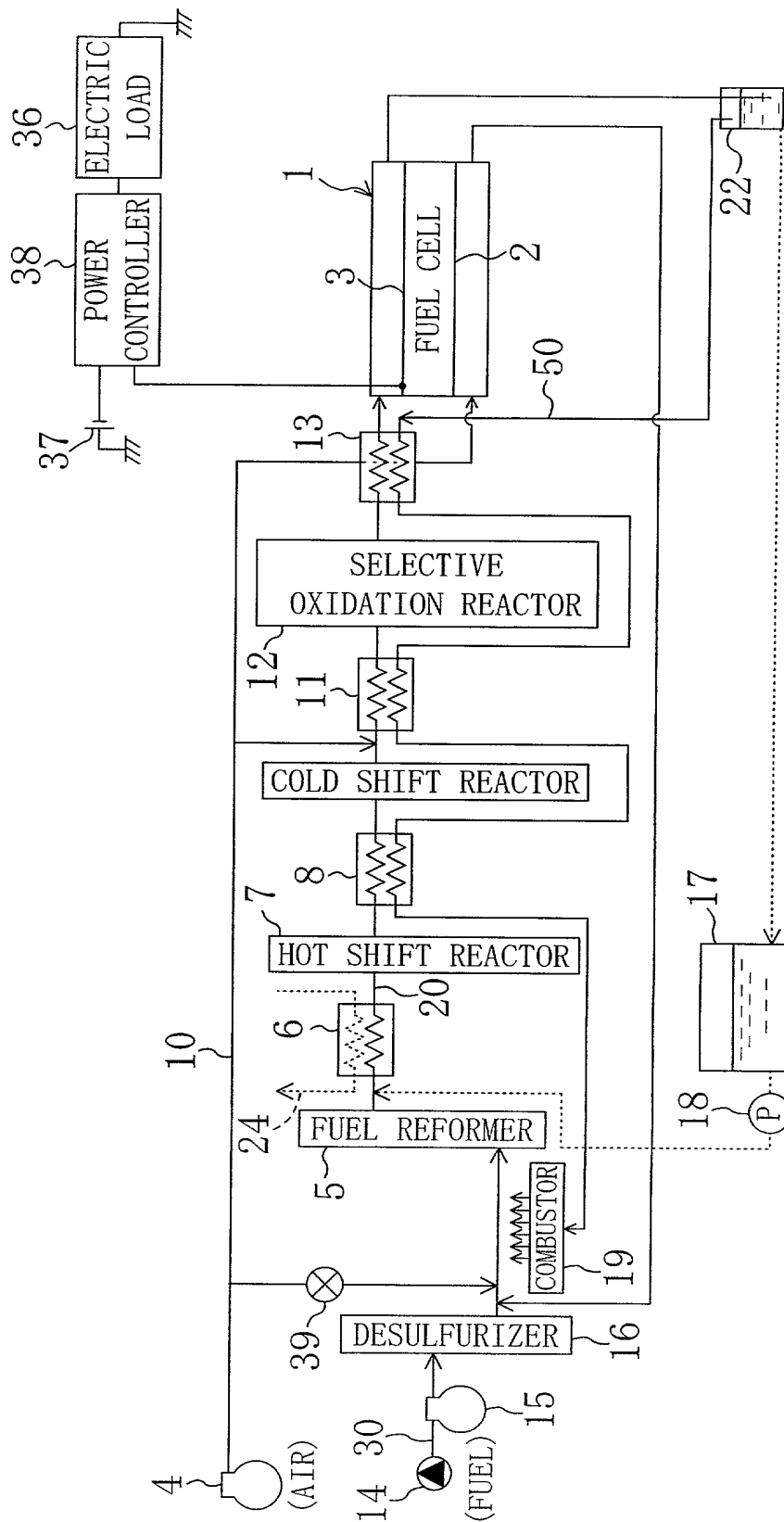
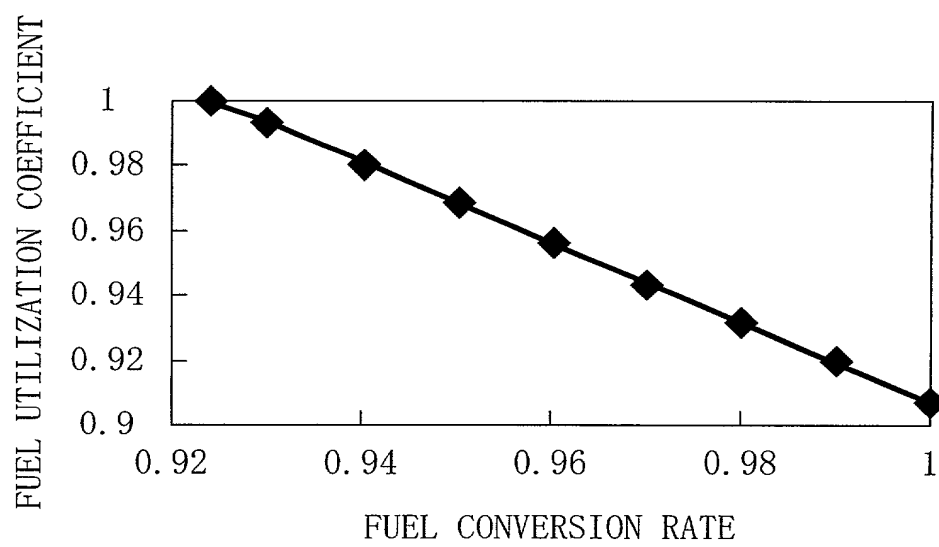


Fig. 4



5/5

Fig. 5



**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

(Includes Reference to PCT International Applications)

Attorney Docket No:

As a below named inventor, I hereby declare that:

My residence post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

HYDROGEN GAS GENERATOR AND FUEL CELL SYSTEM USING

SUCH A GENERATOR

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No.

on

and was amended

on \_\_\_\_\_ (if applicable).

☒ was filed as PCT international application

Number PCT/JP00/06075

on 6 September 2000

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations. § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 of any foreign application(s) for patent or inventor's certificate or of any PCT international applications(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

**PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:**

| COUNTRY | APPLICATION NUMBER | DATE OF FILING<br>(day, month, year) | PRIORITY CLAIMED<br>UNDER 35 USC 119                                |
|---------|--------------------|--------------------------------------|---|
| JAPAN   | 11-257186          | 10/09/1999                           | <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO |
| JAPAN   | 11-257196          | 10/09/1999                           | <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO |
|         |                    |                                      | <input type="checkbox"/> YES <input type="checkbox"/> NO            |
|         |                    |                                      | <input type="checkbox"/> YES <input type="checkbox"/> NO            |
|         |                    |                                      | <input type="checkbox"/> YES <input type="checkbox"/> NO            |

## COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY

(Includes Reference to PCT International Applications)

Attorney Docket No:

I hereby claim the benefit under Title 35, United States Code, § 119(e) or § 120, as applicable of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

## PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120:

## U.S. APPLICATIONS

## STATUS (Check one)

U.S. APPLICATION NUMBER

U.S. FILING DATE

PATENTED

PENDING

ABANDONED

## PCT APPLICATIONS DESIGNATING THE U.S.

PCT APPLICATION NO.

PCT FILING DATE

U.S. SERIAL NUMBERS  
ASSIGNED (if any)

**POWER OF ATTORNEY:** As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number)

Daniel W. Sixbey, (Reg. No. 20,932)

Charles M. Leedom, Jr. (Reg. No. 26,477)

David S. Safran (Reg. No. 27,997)

Donald R. Studebaker (Reg. No. 32,815)

Tim L. Brackett (Reg. No. 36,092)

Robert M. Schulman (Reg. No. 31,196)

Stuart J. Friedman (Reg. No. 24,312)

Gerald J. Ferguson, Jr. (Reg. No. 23,016)

Thomas W. Cole (Reg. No. 28,290)

Jeffrey L. Costellia (Reg. No. 35,483)

Eric J. Robinson (Reg. No. 38,285)

Thomas M. Blasey (Reg. No. 33,475)

Send Correspondence to: Nixon Peabody LLP  
8180 Greensboro Drive, Suite 800  
McLean, Virginia 22102

Direct Telephone Calls to:  
(name and telephone number)

Donald R. Studebaker  
(703) 790-9110

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

The undersigned hereby authorize any U.S. attorney or agent named herein to accept and follow instructions from Maeda Patent Office as to any action to be taken in the Patent and Trademark Office regarding this application without direct communication between the U.S. attorney or agent and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorneys or agents named herein will be so notified by the undersigned.

FULL NAME OF SOLE OR FIRST INVENTOR

INVENTOR'S SIGNATURE

DATE

Nobuki MATSUINobuki Matsui

April 4, 2001

RESIDENCE (City, State &amp; Country)

Osaka, Japan

CITIZENSHIP

Japan

POST OFFICE ADDRESS (Complete Address including City, State &amp; Country)

c/o Kanaoka Factory, Sakai Plant, DAIKIN INDUSTRIES, LTD.,  
1304, Kanaoka-cho, Sakai-shi, Osaka 591-8511, Japan

|  |  |   |                       |
|--|--|---|-----------------------|
| FULL NAME OF SECOND JOINT INVENTOR (if any)<br><b>Shuji IKEGAMI</b>  |  | INVENTOR'S SIGNATURE<br><i>Shuji Ikegami</i>    | DATE<br>April 4, 2001 |
| RESIDENCE (City, State & Country)<br><b>Osaka, Japan JDX</b>   |  | CITIZENSHIP<br><b>Japan</b>                     |                       |
| POST OFFICE ADDRESS (Complete Address including City, State & Country)<br><b>c/o Kanaoka Factory, Sakai Plant, DAIKIN INDUSTRIES, LTD.,<br/>         1304, Kanaoka-cho, Sakai-shi, Osaka 591-8511, Japan</b> |  |   |                       |
| FULL NAME OF THIRD JOINT INVENTOR (if any)<br><b>Yasunori OKAMOTO</b>  |  | INVENTOR'S SIGNATURE<br><i>Yasunori Okamoto</i> | DATE<br>April 4, 2001 |
| RESIDENCE (City, State & Country)<br><b>Osaka, Japan JDX</b>   |  | CITIZENSHIP<br><b>Japan</b>                     |                       |
| POST OFFICE ADDRESS (Complete Address including City, State & Country)<br><b>c/o Kanaoka Factory, Sakai Plant, DAIKIN INDUSTRIES, LTD.,<br/>         1304, Kanaoka-cho, Sakai-shi, Osaka 591-8511, Japan</b> |  |   |                       |
| FULL NAME OF FOURTH JOINT INVENTOR (if any)<br><b>Kazuo YONEMOTO</b>   |  | INVENTOR'S SIGNATURE<br><i>Kazuo Yonemoto</i>   | DATE<br>April 4, 2001 |
| RESIDENCE (City, State & Country)<br><b>Osaka, Japan JDX</b>   |  | CITIZENSHIP<br><b>Japan</b>                     |                       |
| POST OFFICE ADDRESS (Complete Address including City, State & Country)<br><b>c/o Kanaoka Factory, Sakai Plant, DAIKIN INDUSTRIES, LTD.,<br/>         1304, Kanaoka-cho, Sakai-shi, Osaka 591-8511, Japan</b> |  |   |                       |
| FULL NAME OF FIFTH JOINT INVENTOR (if any)   |  | INVENTOR'S SIGNATURE                            | DATE                  |
| RESIDENCE (City, State & Country)  |  | CITIZENSHIP                                     |                       |
| POST OFFICE ADDRESS (Complete Address including City, State & Country)   |  |   |                       |
| FULL NAME OF SIXTH JOINT INVENTOR (if any)   |  | INVENTOR'S SIGNATURE                            | DATE                  |
| RESIDENCE (City, State & Country)  |  | CITIZENSHIP                                     |                       |
| POST OFFICE ADDRESS (Complete Address including City, State & Country)   |  |   |                       |